TITLE OF THE INVENTION:

METHOD FOR ETCHING HIGH DIELECTRIC CONSTANT MATERIALS AND FOR CLEANING DEPOSITION CHAMBERS FOR HIGH DIELECTRIC CONSTANT MATERIALS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation-in-part of U.S. Patent Application No. 10/410,803, filed 10 April 2003, which is a continuation-in-part of U.S. Patent Application No. 10/198,509, filed 18 July 2002, the disclosures of which are incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

[0002] In the manufacture of semiconductor integrated circuits (IC), dielectric materials such as silicon dioxide (SiO_2), silicon nitride (Si_3N_4), and silicon oxynitride (SiON) have been widely used as insulators for transistor gates. Such insulators are often called gate dielectrics. As IC device geometry shrinks, gate dielectric layers have become progressively thinner. When the gate dielectric layer approaches thicknesses of a few nanometers or less, conventional SiO_2, Si_3N_4, and SiON materials undergo electric breakdown and no longer provide insulation. To maintain adequate breakdown voltage at very small thickness ($\leq$ 10 nm), high dielectric constant materials (can be used as the gate insulating layer. The term "high dielectric constant materials" or "high-k materials", as used herein, describe materials where the dielectric constant is greater than about 4.1, or the dielectric constant of silicon dioxide. In addition, high-k materials can also be used as the barrier layer in deep trench capacitors for semiconductor memory chip manufacturing. The IC industry has experimented with many high-k materials. The latest and most promising high-k materials are metal oxides such as Al_2O_3, HfO_2, ZrO_2, and mixtures thereof, and metal silicates such as $HfSi_xO_y$, $ZrSiO_4$, and mixtures thereof. In some instances, nitrogen may be incorporated into these metal oxides and metal silicates high-k materials (such as HfSiON or AlSiON) to improve the dielectric constant and to suppress crystallization of high-k materials. For example, crystallization of high-k materials such as HfO_2 causes high leakage current and device failure. Therefore,

incorporation of nitrogen can dramatically improve the device reliability. In other instances laminate structures of two or more of the above mentioned materials are deposited as the high k dielectric layer. For example, a laminate structure of Al_2O_3 followed by HfO_2 is being employed as the barrier layer in deep trench capacitors.

[0003] High-k materials such as Al_2O_3, HfO_2, and ZrO_2 are very stable and resistive against most of the etching reactions, which has led to their use as etch stop layers and hard mask layers in plasma etching of other materials. See, e.g., K. K. Shih et al., "Hafnium dioxide etch-stop layer for phase-shifting masks", J. Vac. Sci. Technol. B 11(6), pp. 2130-2131 (1993); J. A. Britten, et al., "Etch-stop characteristics of Sc_2O_3 and HfO_2 films for multilayer dielectric grating applications", J. Vac. Sci. Technol. A 14(5), pp. 2973-2975 (1996); J. Hong et al., "Comparison of Cl_2 and F_2 based chemistries for the inductively coupled plasma etching of NiMnSb thin films", J. Vac. Sci. Technol. A 17(4), pp. 1326-1330 (1999); U.S. Patent No. 5,972,722 to Visokay et al.; U.S. Patent No. 6,211,035 B1 to Moise et al., U. S. Patent Application Publication US2001/0055852 A1 to Moise et al.; and EP 1,001,459 A2 to Moise et al.

[0004] These high-k materials are typically deposited from chemical precursors that react in a deposition chamber to form films in a chemical vapor deposition (CVD) process. In some instances, these high-k materials are deposited onto semiconductor substrates (wafers) by atomic layer deposition (ALD), in which the films are deposited in controlled, nearly monoatomic layers. Apparatus and processes for performing ALD are disclosed in, e.g., U.S. Patent No. 5,879,459 to Gadgil et al., U.S. Patent No. 6,174,377 B1 to Doering et al., U.S. Patent Application Publication US2001/0011526 A1 to Doering et al., U.S. Patent No. 6,387,185 B2 to Doering et al., WO 00/40772 to Doering et al. and WO 00/79019 A1 to Gadgil et al. This family of patents assigned to Genus, Inc. teaches that "In situ plasma cleans allow the realization of a very long time between maintenance cleaning." (See, e.g., U.S. Patent No. 6,387,185 B2 at column 7, lines 27-28.) However, no details of any process for plasma cleaning of ALD chambers were given in the above family of disclosures.

[0005] Plasma sources have been used to enhance atomic layer deposition processes (PE-ALD). For example, Pomarede et al. in WO 02/43115 A2 teach the use of plasma sources to generate excited reactive species that prepare/activate the substrate surface to facilitate subsequent ALD. Nguyen et al. in WO 02/43114 A2 teach the use of a pulsing plasma to enact ALD processes instead of alternating precursor chemical flows.

Again, these publications do not disclose any method to clean the ALD residues after the wafers have been processed.

[0006] Although the aforementioned high-k materials are excellent gate insulators, it is very difficult to dry etch these films for pattern transfer. While the deposition process desirably generates high-k films on a substrate (typically a silicon wafer), the reactions that form these films also occur non-productively on other exposed surfaces inside of the deposition chamber. Accumulation of deposition residues results in particle shedding, degradation of deposition uniformity, and processing drifts. These effects can lead to wafer defects and subsequent device failure. Therefore, all CVD chambers, and specifically ALD chambers, must be periodically cleaned.

[0007] Due to their extreme chemical inertness, there have been few attempts to dry etch these high-k materials. J. W. Lee et al. in "Electron cyclotron resonance plasma etching of oxides and SrS and ZnS-based electroluminescent materials for flat panel displays", J. Vac. Sci. Technol. A 16(3), pp. 1944-1948 (1998), reported several chemistries to etch various metal oxides and sulfides. The authors used very powerful plasma conditions (800 W of microwave source power, up to 450 W of RF chuck bias power, and chamber pressure of 1.5 mTorr). The result of such process conditions is very high chuck bias voltage (up to 535 V). High chuck bias voltage can greatly enhance energetic ion sputtering and sputter induced etching. The authors used Cl_2/Ar, BCl_3/Ar, and SF_6/Ar mixture under the extreme plasma conditions to etch various materials. Al_2O_3 showed the slowest etch rates. In most of their experiments, Al_2O_3 etch rates were less than 20% of the ZnS etch rates under identical conditions. The authors also noted "Fairly similar trends were seen with BCl_3/Ar discharges, with the absolute rates being ~20% lower than that for Cl_2/Ar." While the authors' method may be used for anisotropic etching of flat panel display devices, high power plasma sputtering cannot be achieved on grounded chamber surfaces. Therefore, the authors' methods cannot be extended to clean deposition residues within ALD chambers.

[0008] Williams et al. in U.S. Patent 6,238,582 B1 teach a reactive ion beam etching (RIBE) method to etch thin film head materials such as Al_2O_3. The patentees used a CHF_3/Ar plasma as the ion source. A collimated reactive ion beam impinges upon the wafer substrate to etch thin film materials. Such collimated ion beams cannot be used to clean deposition residues from ALD chambers.

[0009] Lagendijk et al. in U.S. Patents Nos. 5,298,075 and 5,288,662 teach a "process for thermal oxidation of silicon or cleaning of furnace tubes ... by exposing the silicon or tube to temperatures above 700°C while flowing a carrier gas containing oxygen and a chlorohydrocarbon having a general formula $C_xH_xCl_x$ where x is 2, 3, or 4 over the silicon or tube. The chlorohydrocarbon is selected to readily and completely oxidize at temperature." (See Abstract.) Oxidation of silicon into SiO_2 and gettering metal contaminants (such as Na and Fe) in oxidation or diffusion furnaces is a completely different process than etching/cleaning high-k materials.

[0010] Various references discuss adding certain compounds to the plasma in order to effect the etch rate of Al_2O_3. The references, W. G. M. Van Den Hoek, "The Etch Mechanism for Al_2O_3 in Fluorine and Chlorine Based RF Dry Etch Plasmas". Met. Res. Soc. Symp. Proc. Vol. 68 (1986), pp. 71-78 and Heiman, et al., "High Rate Reactive Ion Etching of Al_2O_3 and Si", J. Vac. Sci. Tech., 17(3), May/June 1980, pp. 731-34, disclose adding a fluorine based gas or a chlorine based gas, respectively, to an Ar plasma to increase the etch rate of Al_2O_3. However, these studies were all under the reactive ion etch (RIE) conditions. Ion bombardment/sputter induced reactions play a much large role than chemical etching reactions. Like other prior arts, such extreme RIE conditions do not apply to cleaning grounded chamber surfaces.

[0011] In view of the dearth of art disclosing methods for removing high-k dielectric residues, ALD reactors have typically been cleaned by mechanical means (scrubbing or blasting) to clean up the deposition residues from the internal surfaces of the chamber and downstream equipment (e.g. pump headers and exhaust manifolds). However, mechanical cleaning methods are time-consuming, labor-intensive, and damaging to the surfaces being cleaned.

[0012] Fluorine-containing plasma-based processes (i.e., dry cleaning) are commonly used to remove residues of silicon compounds (such as polycrystalline silicon, SiO_2, SiON, and Si_3N_4) and tungsten from the interior surfaces of chemical vapor deposition (CVD) reactors. Here, fluorine reacts with the aforementioned residues to produce, for example, SiF_4 or WF_6, volatile species that can be pumped out of the reactor during the cleaning process. However, fluorine-based chemistry alone is ineffective to remove the high-k dielectric materials discussed above. See, e.g., J. Hong et al., J. Vac. Sci. Technol. A, Vol. 17, pp1326-1330, 1999, wherein the authors exposed Al_2O_3 coated wafers to NF_3/Ar based inductively coupled plasmas, and found that "the greater

concentration of atomic F available at high source power contributed to thicker fluorinated surfaces, leading to the net deposition rather than etching." In the case of high-k materials the metal fluoride product that forms is nonvolatile and, thus, difficult to remove from the reactor.

[0013] Thus, there is an urgent need for a process to chemically dry clean high-k material residues, such as Al_2O_3, HfO_2, ZrO_2, $HfSi_xO_y$, $ZrSi_xO_y$ and mixtures thereof, residues of laminates containing high-k materials such as HfO_2 and Al_2O_3 (also referred to as HfAlO), and residues from nitrogen containing high-k material such as HfON, AlON, and laminated materials between HfON and AlON (HfAlON), from ALD chambers without venting/opening up the chamber. An effective chemical dry cleaning method will significantly increase the productivity and lower the cost-of-ownership (CoO) for ALD-based deposition processes.

[0014] All references cited herein are incorporated herein by reference in their entireties.

BRIEF SUMMARY OF THE INVENTION

[0015] A process for removing a substance from a substrate and a mixture for accomplishing the same are disclosed herein. In one aspect, there is provided a process for cleaning a substance from a reactor surface comprising: providing a reactor containing the reactor surface, wherein: (a) the reactor surface is at least partially coated with a film of the substance; (b) the substance is at least one member selected from the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing Group 13 metal oxide, a nitrogen containing Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, or a laminate comprising at least one layer selected from the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, a nitrogen containing Group 13 metal oxide, or a nitrogen containing Group 13 metal silicate; and (c) the substance has a dielectric constant greater than the dielectric constant of silicon dioxide; reacting the substance with a reactive agent to form a volatile product, wherein the reactive agent comprises at least one member selected from the group consisting of a halogen-containing compound; a boron-containing compound, a carbon-containing compound, a

hydrogen-containing compound, a nitrogen-containing compound, a chelating compound, a chlorosilane compound, a hydrochlorosilane compound, or an organochlorosilane compound; and removing the volatile product from the reactor to thereby remove the substance from the surface.

[0016] In another aspect, there is provided a process for removing a substance from a surface of a reaction chamber comprising: providing a reaction chamber wherein at least a portion of the surface is at least partially coated with the substance and wherein the substance has a dielectric constant of 4.1 or greater and is at least one member of the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing Group 13 metal oxide, a nitrogen containing Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, or a laminate comprising at least one layer of the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing Group 13 metal oxide, a nitrogen containing Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate; introducing a reactive agent into the reaction chamber wherein the reactive agent comprises at least one member selected from the group consisting of a halogen-containing compound; a boron-containing compound, a carbon-containing compound, a hydrogen-containing compound, a nitrogen-containing compound, a chelating compound, a chlorosilane compound, a hydrochlorosilane compound, or an organochlorosilane compound; exposing the reactive agent to one or more energy sources sufficient to react the substance with the reactive agent and form a volatile product; and removing the volatile product from the reaction chamber.

[0017] In yet another aspect of the present invention, there is provided an apparatus for removing a substance from at least one surface of a reactor comprising: an at least one reactive agent selected from the group consisting of a halogen-containing compound; a boron-containing compound, a carbon-containing compound, a hydrogen-containing compound, a nitrogen-containing compound, a chelating compound, a chlorosilane compound, a hydrochlorosilane compound, or an organochlorosilane compound; and a non-reactive support having the at least one reactive agent deposited thereupon.

[0018] In a further aspect of the present invention, there is provided a mixture for removing a substance from at least one surface of a reactor comprising: an at least one reactive agent selected from the group consisting of a halogen-containing compound; a boron-containing compound, a carbon-containing compound, a hydrogen-containing compound, a nitrogen-containing compound, a chelating compound, a chlorosilane compound, a hydrochlorosilane compound, or an organochlorosilane compound; and an inert diluent.

[0019] In yet another aspect of the present invention, there is provided a process for removing a substance from an at least one surface of a substrate comprising: providing the substrate wherein the substrate is at least partially coated with a film of the substance that is at least one member selected from the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide other than Al_2O_3, a Group 13 metal silicate, a nitrogen containing Group 13 metal oxide, a nitrogen containing Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, or a laminate comprising at least one layer of the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing Group 13 metal oxide, a nitrogen containing Group 13 metal silicate, a nitrogen containing transition metal oxide, or a nitrogen containing transition metal silicate; and wherein the substance has a dielectric constant greater than a dielectric constant of silicon dioxide; reacting the substance with a reactive agent to form a volatile product, wherein the reactive agent comprises at least one member from the group consisting of a halogen-containing compound ; a boron-containing compound, a carbon-containing compound, a hydrogen-containing compound, a nitrogen-containing compound, a chelating compound, a chlorosilane compound, a hydrochlorosilane compound, or an organochlorosilane compound; and removing the volatile product from the substrate to thereby remove the substance from the substrate.

[0020] In yet another aspect of the present invention, there is provided a process for cleaning a substance from a reactor surface comprising: providing a reactor containing the reactor surface, wherein: (a) the reactor surface is at least partially coated with a film of the substance; (b) the substance silicate; and oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing Group 13 metal oxide, a nitrogen containing Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, or a laminate comprising at

least one layer selected from the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, a nitrogen containing Group 13 metal oxide, or a nitrogen containing Group 13 metal silicate; and (c) the substance has a dielectric constant greater than the dielectric constant of silicon dioxide; reacting the substance with a reactive agent comprising at least one fluorine-containing compound and at least one selected from a chlorine-containing compound, a bromine-containing compound, or a iodine-containing compound wherein the fluorine-containing compound is less than 50% by volume of an amount of the reactive agent; and removing the volatile product from the reactor to thereby remove the substance from the surface.

[0021] These and other aspects of the invention will become apparent from the following detailed description.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

[0022] Figures 1a and 1b provides an illustration of an apparatus suitable for performing chamber cleaning using an internal energy source or a remote energy source, respectively.

[0023] Figure 2 provides an illustration of an apparatus for performing a process of the invention using plasma as the energy source.

[0024] Figure 3 provides a graphical illustration of the relative BCl_3 plasma etch rates of various high dielectric constant materials, normalized to Al_2O_3.

[0025] Figure 4 provides an illustration of an apparatus for performing a process of the invention using thermal heating as the energy source

[0026] Figure 5 provides an illustration of the etch rate dependence on lower electrode/pedestal set temperature at constant chamber pressure and BCl_3 flow rate.

[0027] Figure 6 provides an illustration of the etch rate dependence on chamber pressure at constant lower electrode set temperature and BCl_3 flow rate.

[0028] Figures 7a through 7c illustrate the HfO_2, $HfSi_xO_y$, and ZrO_2 etch rates, respectively, at different NF_3 percentages in the mixture of BCl_3 and NF_3 for one embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0029] The present process is useful for dry-etching high-k materials and dry-cleaning chemical vapor deposition (CVD) chambers (and more specifically, ALD chambers) used to deposit high-k materials onto wafer surfaces. The material to be removed from the surface being etched or cleaned is converted from a solid non-volatile material into materials having higher volatility than the high-k materials deposited thereupon and can be subsequently removed, for example, by reactor vacuum pumps. Thus, the invention removes a substance from a substrate using one or more reactive agents to volatilize the substance. Unlike wet-etching and wet-cleaning processes, dry-etching and dry-cleaning processes do not immerse the substrate in or expose the substrate to liquid chemical solutions.

[0030] In certain embodiments, the substance to be removed can be a transition metal oxide, a transition metal silicate, a Group 13 metal oxide or a Group 13 metal silicate (in accordance with the IUPAC Nomenclature of Inorganic Chemistry, Recommendations 1990, Group 13 metals include Al, Ga, In and Tl, and the transition metals occupy Groups 3-12). The substance may be a high-k material having a dielectric constant greater than that of silicon dioxide (i.e., greater than about 4.1), or greater than 5, or at least 7. Preferably, the substance is at least one member selected from the group consisting of Al_2O_3, HfO_2, ZrO_2, $HfSi_xO_y$, $ZrSi_xO_y$, and mixtures thereof. Those skilled in the art will appreciate that the formula $HfSi_xO_y$ (and the formula $ZrSi_xO_y$) represents a mixture of HfO_2 (ZrO_2) and SiO_2, where x is greater than 0 and y is 2x + 2.

[0031] In other embodiments of the present invention, the substance may be a laminate comprising layers of at least one member selected from the group of the following materials: a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, a nitrogen containing Group 13 metal oxide, or a nitrogen containing Group 13 metal silicate. The laminate is preferably alternating between at least one of the foregoing materials and, optionally, other materials such as insulating materials. For example, the laminate may be comprised of alternating layers of HfO_2 and Al_2O_3. The laminate may also consist of a certain number of layers of a first material and a certain number of layers of a second material or, alternatively, outer layers of at least one first material and inner layers of at least one second material.

[0032] In yet a further embodiment of the present invention, the substance may be a nitrogen containing material such as a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, a nitrogen containing Group 13 metal oxide, or a nitrogen containing Group 13 metal silicate. An example of this type of substance includes HfAlON.

[0033] As mentioned previously, the substance to be removed is reacted with a reactive agent to form a volatile product which can be readily removed from the substrate. In certain preferred embodiments, the reactive agent may be exposed to one or more energy sources sufficient to form active species such as ions, radicals, excited neutrals, and the like, which react with the substance and form the volatile product. Examples of suitable reactive agents include: a halogen-containing compound such as a chloride, bromide, fluoride, or iodide compound; a boron-containing compound, a carbon-containing compound, a hydrogen-containing compound, a nitrogen-containing compound , a chelating compound, a chlorosilane compound, a hydrochlorosilane compound, an organochlorosilane compound, or a mixture thereof. Although the reactive agents used herein may be sometimes described as "gaseous", it is understood that the chemical reagents may be delivered directly as a gas to the reactor, delivered as a vaporized liquid, a sublimed solid and/or transported by an inert diluent gas into the reactor.

[0034] The reactive agents can be delivered to the reaction chamber by a variety of means, such as, for example, conventional cylinders, safe delivery systems, vacuum delivery systems, solid or liquid-based generators that create the reactive agent at the point of use. In one embodiment of the present invention, at least one reactive agent can be added to a non-reactive liquid or gaseous diluent and applied to the substrate having the substance to be removed as a spray or other means. The reactive agent can react with the substance to form the volatile product upon exposure to one or more energy sources. In an alternative embodiment such as for chamber cleaning applications, the reactive agent(s) can be deposited onto a non-reactive support which can be introduced into the reaction chamber. The material of the non-reactive support is one that will not react with the reactive agent prior to or during exposure to one of energy sources. In certain preferred embodiments, the non-reactive support has a plurality of pores. The reactive agent(s) can be released upon exposure to one or more energy sources and react with the substance to be removed to form the volatile product.

[0035] Since the chlorides of these metals (such as $AlCl_3$, $HfCl_4$, $ZrCl_4$, and $SiCl_4$) are more volatile, it may be preferrable to convert these high-k substances into chlorides. This conversion is accomplished by contacting the substance to be removed with a reactive agent containing chlorine. Examples of chlorine-containing reactive agents include BCl_3, $COCl_2$, HCl, Cl_2, ClF_3, and NF_zCl_{3-z}, where z is an integer from 0 to 2, chlorocarbons, and chlorohydrocarbons (such as $C_xH_yCl_z$ where x is a number ranging from 1 to 6, y is a number ranging from 0 to 13, and z is a number ranging from 1 to 14). Chlorine-containing reactive agents that also contain oxygen-getter functions, such as BCl_3, $COCl_2$, chlorocarbons and chlorohydrocarbons, may be suitable in certain embodiments because the oxygen-getter component (B, CO, C, or H) in these molecules extracts oxygen from the high-k materials and hence enhances the conversion of metal oxides and metal silicates into metal chlorides. Among the chlorine-containing and oxygen-getter gases, BCl_3 is the most preferred one. In embodiments employing $COCl_2$ as the reactive agent it can be provided in prepared form or formed by an in situ reaction of CO and Cl_2. In certain embodiments, the reactive agent can comprise a chlorine-containing gas and a fluorine-containing gas (e.g., BCl_3 and BF_3), or a gas containing both fluorine and chlorine such as ClF_3, and NF_zCl_{3-z}, where z is an integer from 0 to 2.

[0036] In alternative embodiments, one or more chlorine-containing reactive agents can be combined with one or more other halogen-containing compounds such as one or more fluorine-containing reactive agents to aid in etching and removing high-k materials. Although the fluorides of transition metals such HfF_4 and ZrF_4 are less volatile than the corresponding chlorides, it is surprising and unexpected that adding at least one fluorine-containing reactive agent to chlorine-containing reactive agent may enhance the etch rate of high dielectric constant transition metal oxides. In these embodiments, the gaseous mixture may comprise less than 50% by volume of at least one fluorine-containing reactive agent; at least one chlorine-containing reactive agent; and optionally inert diluent gas. An exemplary gas mixture may comprise from about 1% to less than 50% by volume of at least one fluorine-containing compound and from about 50% to about 99% by volume of at least one chlorine-containing compound. The fluorine-containing reactive agent(s) may be combined with the chlorine-containing reactive agent(s) to provide the mixture prior to or after introduction to the reactor. Examples of suitable fluorine-containing reactive agents include NF_3 (nitrogen trifluoride), ClF_3 (chlorine trifluoride), ClF (chlorine fluoride), SF_6 (sulfur hexafluoride), perfluorocarbons such as CF_4 and C_2F_6 etc, hydrofluorocarbons such as CHF_3 and C_3F_7H etc.,

oxyfluorocarbons such as C_4F_8O (perfluorotetrahydrofuran) etc., hypofluorites such as CF_3-OF (fluoroxytrifluoromethane (FTM)) and FO-CF_2-OF (bis-difluoroxy-difluoromethane (BDM)) etc., fluoroperoxides such as CF_3-O-O-CF_3, F-O-O-F etc., fluorotrioxides such as CF_3-O-O-O-CF_3 etc., COF_2 (carbonyl flouride), NOF, NF_xCl_{3-x}, where x is an integer from 1 to 2, and F_2 etc. Exemplary gaseous mixtures include, but are not limited to, BCl_3 and NF_3; BCl_3 and F_2; BCl_3 and ClF_3; BCl_3 and NF_xCl_{3-x} where x is an integer from 1 to 2. Other Cl-, Br-, or I- containing compounds such as, for example, any of the compounds disclosed herein, may also have this synergistic effect with the F-containing compounds.

[0037] In addition to the reactive agents described herein, inert diluent gases such as nitrogen, CO, helium, neon, argon, krypton, and xenon etc. can also be added. Inert diluent gases can modify the plasma characteristics and cleaning processes to better suit some specific applications. The concentration of the inert gases can range from 0 to 99%.

[0038] The process of the invention is useful for etching substances from the surfaces of a substrate. Thus, suitable substrates for the etching embodiments of the invention include, e.g., semiconductor wafers and the like. Figure 3 shows a comparison of the relative etch rate of hafnium oxide, aluminum oxide, and zirconium oxide for one embodiment of the present invention using BCl_3 as the reactive agent.

[0039] The present invention may be also suitable for cleaning substances from substrates such as surfaces of reaction chambers for CVD and/or ALD processes. The present invention is particularly suited for removing high k substances that have deposited onto the exposed surfaces of a reaction chamber such as, for example, the workpiece platform, grounded sidewalls, and/or showerhead of a typical reaction chamber.

[0040] The one or more reactive agents are exposed to one or more energy sources sufficient to generate active species to at least partially react with the substance and/or boron-containing by-products and form volatile species. The energy source for the exposing step may include, but not be limited to, α-particles, β-particles, γ-rays, x-rays, high energy electron, electron beam sources of energy; ultraviolet (wavelengths ranging from 10 to 400 nm), visible (wavelengths ranging from 400 to 750 nm), infrared (wavelengths ranging from 750 to 10^5 nm), microwave (frequency > 10^9 Hz), radio-

frequency wave (frequency > 10^6 Hz) energy; thermal; RF, DC, arc or corona discharge; sonic, ultrasonic or megasonic energy; and mixtures thereof.

[0041] In certain embodiments, thermal or plasma activation and/or enhancement can significantly impact the efficacy of dry etching and dry cleaning of high dielectric constant materials. For thermal activation, the substrate can be heated up to 600°C, or up to 400°C, or up to 300°C. The pressure range is generally 10 mTorr to 760 Torr, or 1 Torr to 760 Torr.

[0042] In alternative embodiments, the reactive agent(s) are activated by a plasma in situ or within the reactor containing the substance to be removed. For in situ plasma activation, one can generate the plasma with a 13.56 MHz RF power supply, with RF power density at least 0.2 W/cm^2, or at least 0.5 W/cm^2, or at least 1 W/cm^2. One can also operate the in situ plasma at RF frequencies lower than 13.56 MHz to enhance ion assisted cleaning of grounded ALD chamber walls. The operating pressure is generally in the range of 2.5 mTorr to 100 Torr, or 5 mTorr to 50 Torr, or 10 mTorr to 20 Torr. Optionally, one can also combine thermal and plasma enhancement for more effective cleaning of ALD chamber walls.

[0043] One can also use a remote plasma source to replace an in situ plasma to generate more reactive species. The remote plasma source can be generated by either an RF or a microwave source. In addition, reactions between remote plasma generated reactive species and high-k materials can be activated/enhanced by heating ALD reactor components to elevated temperatures up to 600°C, or to 400°C, or up to 300°C.

[0044] Other means of activation and enhancement to the cleaning processes can also be employed. For example, one can use photon induced chemical reactions to generate reactive species and enhance the etching/cleaning reactions.

[0045] The following tables show thermochemical calculations for various reactions for volatilizing the substance to be removed from the substrate. In these tables, K_{eq} represents the equilibrium constant for the reaction as written; so that the larger this value is, the more favorable the reaction will be to proceed.

Table 1. Al_2O_3 reaction with BCl_3: $Al_2O_3 + 2BCl_3(g) \leftrightarrow B_2O_3 + 2AlCl_3(g)$

Temperature (°C)	ΔH (Kcal)	ΔS (Cal)	ΔG (Kcal)	K_{eq}
0.000	9.561	12.274	6.208	1.078E-005
100.000	9.547	12.249	4.976	1.217E-003
200.000	9.424	11.959	3.766	1.822E-002
300.000	9.299	11.719	2.582	1.036E-001
400.000	9.196	11.553	1.419	3.461E-001
500.000	15.123	19.739	-0.138	1.094E+000
600.000	15.476	20.169	-2.135	3.422E+000
700.000	15.748	20.464	-4.167	8.629E+000
800.000	15.951	20.664	-6.224	1.852E+001
900.000	16.097	20.794	-8.298	3.515E+001
1000.000	16.190	20.871	-10.381	6.056E+001

Table 2. HfO_2 reaction with BCl_3: $1.5HfO_2 + 2BCl_3(g) \leftrightarrow 1.5HfCl_4(g) + B_2O_3$

Temperature (°C)	ΔH (Kcal)	ΔS (Cal)	ΔG (Kcal)	K_{eq}
0.000	-17.999	-12.638	-14.547	4.367E+011
25.000	-18.003	-12.653	-14.231	2.707E+010
50.000	-18.025	-12.721	-13.914	2.576E+009
75.000	-18.057	-12.817	-13.595	3.426E+008
100.000	-18.096	-12.924	-13.273	5.950E+007
125.000	-18.138	-13.034	-12.948	1.283E+007
150.000	-18.182	-13.141	-12.621	3.305E+006
175.000	-18.226	-13.242	-12.291	9.879E+005
200.000	-18.268	-13.335	-11.959	3.346E+005

Table 3. ZrO_2 reaction with BCl_3: $1.5ZrO_2 + 2BCl_3(g) \leftrightarrow 1.5ZrCl_4(g) + B_2O_3$

Temperature (°C)	ΔH (Kcal)	ΔS (Cal)	ΔG (Kcal)	K_{eq}
0.000	-29.845	-12.107	-26.538	1.717E+021
25.000	-29.825	-12.038	-26.236	1.710E+019
50.000	-29.822	-12.026	-25.935	3.481E+017
75.000	-29.828	-12.047	-25.634	1.239E+016
100.000	-29.842	-12.083	-25.333	6.891E+014
125.000	-29.858	-12.126	-25.030	5.502E+013
150.000	-29.875	-12.168	-24.726	5.913E+012
175.000	-29.892	-12.207	-24.422	8.142E+011
200.000	-29.908	-12.240	-24.116	1.381E+011

Table 4. HfO_2 reaction with $COCl_2$: $HfO_2 + 2COCl_2(g) \leftrightarrow HfCl_4(g) + 2CO_2(g)$

Temperature (°C)	ΔH (Kcal)	ΔS (Cal)	ΔG (Kcal)	K_{eq}
0.000	-20.643	41.960	-32.105	4.890E+025
25.000	-20.649	41.940	-33.153	2.014E+024
50.000	-20.668	41.878	-34.201	1.357E+023
75.000	-20.699	41.787	-35.247	1.343E+022
100.000	-20.739	41.677	-36.290	1.806E+021
125.000	-20.786	41.554	-37.331	3.112E+020
150.000	-20.840	41.423	-38.368	6.578E+019
175.000	-20.900	41.285	-39.402	1.647E+019
200.000	-20.965	41.144	-40.432	4.757E+018

Table 5. ZrO_2 reaction with $COCl_2$: $ZrO_2 + 2COCl_2(g) \leftrightarrow ZrCl_4(g) + 2CO_2(g)$

Temperature (°C)	ΔH (Kcal)	ΔS (Cal)	ΔG (Kcal)	K_{eq}
0.000	-28.540	42.313	-40.098	1.218E+032
25.000	-28.530	42.350	-41.157	1.483E+030
50.000	-28.533	42.341	-42.215	3.573E+028
75.000	-28.547	42.300	-43.273	1.469E+027
100.000	-28.569	42.238	-44.330	9.244E+025
125.000	-28.599	42.160	-45.385	8.215E+024
150.000	-28.636	42.071	-46.438	9.694E+023
175.000	-28.678	41.975	-47.489	1.448E+023
200.000	-28.724	41.873	-48.537	2.638E+022

Table 6. $ZrSiO_4$ reaction with BCl_3:
$ZrSiO_4 + 2.667BCl_3(g) \leftrightarrow SiCl_4(g) + ZrCl_4(g) + 1.333B_2O_3$

Temperature (°C)	ΔH (Kcal)	ΔS (Cal)	ΔG (Kcal)	K_{eq}
0.000	-31.065	-21.096	-25.303	1.764E+020
25.000	-31.003	-20.879	-24.778	1.460E+018
50.000	-30.962	-20.747	-24.258	2.554E+016
75.000	-30.935	-20.665	-23.740	8.020E+014
100.000	-30.916	-20.613	-23.224	4.013E+013
125.000	-30.902	-20.577	-22.710	2.928E+012
150.000	-30.891	-20.549	-22.196	2.914E+011
175.000	-30.879	-20.523	-21.682	3.755E+010
200.000	-30.867	-20.496	-21.169	6.012E+009
225.000	-30.852	-20.466	-20.657	1.158E+009
250.000	-30.835	-20.432	-20.146	2.612E+008
275.000	-30.814	-20.393	-19.636	6.754E+007
300.000	-30.790	-20.349	-19.127	1.967E+007
325.000	-30.761	-20.300	-18.618	6.358E+006
350.000	-30.729	-20.247	-18.112	2.252E+006
375.000	-30.692	-20.190	-17.606	8.652E+005
400.000	-30.652	-20.130	-17.102	3.572E+005
425.000	-30.608	-20.066	-16.600	1.573E+005
450.000	-22.891	-9.391	-16.100	7.349E+004
475.000	-22.663	-9.081	-15.869	4.327E+004
500.000	-22.443	-8.791	-15.646	2.649E+004

Table 7. $ZrSiO_4$ reaction with BF_3 and BCl_3:
$ZrSiO_4 + 1.333BF_3(g) + 1.333BCl_3(g) \leftrightarrow SiF_4(g) + ZrCl_4(g) + 1.333B_2O_3$

Temperature (°C)	ΔH (Kcal)	ΔS (Cal)	ΔG (Kcal)	K_{eq}
0.000	-25.010	-21.014	-19.270	2.627E+015
25.000	-24.951	-20.807	-18.748	5.540E+013
50.000	-24.912	-20.681	-18.229	2.136E+012
75.000	-24.885	-20.600	-17.713	1.319E+011
100.000	-24.865	-20.545	-17.199	1.186E+010
125.000	-24.849	-20.502	-16.686	1.445E+009
150.000	-24.833	-20.463	-16.174	2.260E+008
175.000	-24.816	-20.423	-15.663	4.354E+007
200.000	-24.796	-20.380	-15.153	9.992E+006
225.000	-24.772	-20.332	-14.644	2.661E+006
250.000	-24.745	-20.278	-14.136	8.053E+005
275.000	-24.712	-20.218	-13.630	2.721E+005
300.000	-24.675	-20.152	-13.125	1.012E+005
325.000	-24.633	-20.080	-12.622	4.095E+004
350.000	-24.586	-20.003	-12.121	1.784E+004
375.000	-24.535	-19.922	-11.622	8.303E+003
400.000	-24.478	-19.837	-11.125	4.095E+003
425.000	-24.418	-19.749	-10.630	2.128E+003
450.000	-16.684	-9.050	-10.139	1.160E+003
475.000	-16.439	-8.717	-9.917	7.894E+002
500.000	-16.201	-8.405	-9.703	5.535E+002

[0046] Tables 1-7 show that BCl_3 and $COCl_2$ can be used as the etchants for dry etching and cleaning of the high-k materials. BCl_3 (boron trichloride) is a liquefied gas at room temperature and can be readily delivered into ALD reactors for chamber cleaning. $COCl_2$ (phosgene) is preferably provided in situ in etch or deposition reactors by reacting gaseous carbon monoxide and chlorine to form phosgene assisted by an external energy source (e.g. plasma) as follows:

$$CO\ (g) + Cl_2\ (g) \rightarrow COCl_2$$

[0047] In other embodiments of the present invention such as applications that are sensitive to boron residue, chlorocarbons (CC) and hydrochlorocarbons (HCC) may be employed as the reactive agent because these compounds may contain chlorine as well as oxygen getter components (C or H). The general formula for the CC and HCC compounds is $C_xH_yCl_z$, where x ranges from 1 to 6, y ranges from 0 to 13, and z ranges from 1 to 14. Examples of suitable CC and HCC compounds include, but are not limited to, trans-dichloroethylene $C_2H_2Cl_2$ (a.k.a. Trans-LC®), cis-dichloroethylene, 1,1-dichloroethylele, 1,1,1-trichloroethane ($C_2H_3Cl_3$), or tetrachloroethylene C_2Cl_4, $C_4H_4Cl_4$,

$CHCl_3$, and CCl_4. Some CC and HCC compounds may react with high-k metal oxides without the addition of oxygen. For example, in some embodiments, tetrachloroethylene (C_2Cl_4) can react with Al_2O_3 to form volatile byproducts as follows:

$$1.5C_2Cl_4(g) + Al_2O_3 \rightarrow 2AlCl_3(g) + 3CO(g)$$

Table 8 illustrates that the reaction is thermodynamically favorable at temperatures above 100 °C.

Table 8. Thermodynamic data for reaction:
$1.5C_2Cl_4(g) + Al_2O_3 = 2AlCl_3(g) + 3CO(g)$

T (°C)	ΔH (kcal)	ΔS (cal)	ΔG (kcal)	K_{eq}
0.000	46.723	157.382	3.734	1.028E-003
100.000	46.760	157.552	-12.031	1.114E+007
200.000	46.314	156.508	-27.738	6.509E+012
300.000	45.599	155.144	-43.322	3.317E+016
400.000	44.704	153.709	-58.765	1.204E+019
500.000	43.674	152.284	-74.064	8.667E+020
600.000	42.541	150.907	-89.223	2.160E+022
700.000	41.340	149.605	-104.248	2.594E+023
800.000	40.087	148.380	-119.147	1.848E+024
900.000	38.793	147.228	-133.927	8.948E+024
1000.000	37.467	146.143	-148.595	3.236E+025

[0048] The above thermochemical calculations are illustrations of limiting cases for those chemical reactions. In addition to the limiting case reaction products such as B_2O_3, intermediate reaction products such as boron oxychloride (BOCl) can also be formed in reactions between high-k materials and BCl_3. Intermediate reaction products such as BOCl may have higher volatility and thus may further enhance the removal of high-k materials.

[0049] Other CC and HCC compounds may need the addition of oxygen to release chlorine without forming carbon residues (soot). For example, trans-dichloroethylene ($C_2H_2Cl_2$) (a.k.a. Trans-LC®) can react with Al_2O_3 at an O_2:$C_2H_2Cl_2$ molar ratio of 2:1:

$$6O_2(g) + Al_2O_3 + 3C_2H_2Cl_2(g) = 2AlCl_3(g) + 6CO_2(g) + 3H_2O(g)$$

Table 9 shows such a reaction is thermodynamically favorable at temperatures between 0 and 1000 °C.

Table 9 Thermodynamic data for reaction:
$6O_2(g) + Al_2O_3 + 3C_2H_2Cl_2(g) = 2AlCl_3(g) + 6CO_2(g) + 3H_2O(g)$

T (°C)	ΔH (kcal)	ΔS (kcal)	ΔG (kcal)	K_{eq}
0.000	-616.464	77.981	-637.764	1.000E+308
100.000	-616.428	78.113	-645.576	1.000E+308
200.000	-616.656	77.585	-653.365	6.559E+301
300.000	-617.145	76.654	-661.079	1.257E+252
400.000	-617.872	75.490	-668.688	1.316E+217
500.000	-618.811	74.193	-676.173	1.422E+191
600.000	-619.918	72.848	-683.525	1.261E+171
700.000	-621.140	71.523	-690.743	1.380E+155
800.000	-622.440	70.253	-697.832	1.340E+142
900.000	-623.784	69.056	-704.796	2.040E+131
1000.000	-625.138	67.947	-711.646	1.485E+122

[0050] An excess amount of oxygen is undesirable in the above reactions since excess O_2 can convert metal chlorides back to metal oxides. A better way to prevent excess oxygen is to oxidize carbon only partially into CO by running the reaction under an oxygen lean condition. For example, O_2:$C_2H_2Cl_2$ molar ratio of 1:1 can lead to the formation of CO and $AlCl_3$ as the byproducts:

$$3C_2H_2Cl_2(g) + Al_2O_3 + 3O_2 = 2AlCl_3(g) + 6CO(g) + 3H_2O(g)$$

As shown in Table 10, such partial oxidation reaction is also favorable thermodynamically.

Table 10 Thermodynamic data for reaction:
$3C_2H_2Cl_2(g) + Al_2O_3 + 3O_2 = 2AlCl_3(g) + 6CO(g) + 3H_2O(g)$

T (°C)	ΔH (kcal)	ΔS (kcal)	ΔG (kcal)	K_{eq}
0.000	-210.973	200.961	-265.865	5.480E+212
100.000	-210.103	203.760	-286.136	3.984E+167
200.000	-210.055	203.905	-306.532	3.982E+141
300.000	-210.561	202.949	-326.881	4.512E+124
400.000	-211.485	201.470	-347.105	5.046E+112
500.000	-212.749	199.725	-367.166	6.267E+103
600.000	-214.276	197.870	-387.046	7.688E+096
700.000	-215.992	196.011	-406.740	2.255E+091
800.000	-217.847	194.197	-426.250	6.518E+086
900.000	-219.797	192.461	-445.582	1.037E+083
1000.000	-221.800	190.822	-464.745	6.097E+079

[0051] Instead of oxygen, chlorine (Cl_2) can be added to prevent the formation of carbon soot. For example, Cl_2:$C_2H_2Cl_2$ molar ratio of 2:1 allows the following reaction:

$$2Cl_2(g) + Al_2O_3 + C_2H_2Cl_2(g) = 2AlCl_3(g) + H_2O(g) + 2CO(g)$$

Similarly, Cl_2:$C_2H_2Cl_2$ molar ratio of 4:1 allows the following reaction:

$$4Cl_2(g) + Al_2O_3 + C_2H_2Cl_2(g) = 3.333AlCl_3(g) + H_2O(g) + 2CO_2(g)$$

Both reactions are thermodynamically favorable, as shown in Tables 11 and 12. The use of chlorine to control soot formation is more desirable since excess amount of chlorine helps the chlorination of metal oxides.

Table 11 Thermodynamic data for reaction:
$2Cl_2(g) + Al_2O_3 + C_2H_2Cl_2(g) = 2AlCl_3(g) + H_2O(g) + 2CO(g)$

T (°C)	ΔH (kcal)	ΔS (kcal)	ΔG (kcal)	K_{eq}
0.000	10.291	101.403	-17.407	8.479E+013
100.000	10.619	102.465	-27.616	1.498E+016
200.000	10.554	102.326	-37.861	3.088E+017
300.000	10.225	101.701	-48.065	2.135E+018
400.000	9.697	100.855	-58.194	7.859E+018
500.000	9.005	99.900	-68.233	1.946E+019
600.000	8.185	98.904	-78.173	3.701E+019
700.000	7.277	97.920	-88.014	5.858E+019
800.000	6.303	96.967	-97.758	8.134E+019
900.000	5.280	96.056	-107.409	1.026E+020
1000.000	4.224	95.193	-116.971	1.205E+020

Table 12 Thermodynamic data for reaction:
$4Cl_2(g) + Al_2O_3 + C_2H_2Cl_2(g) = 3.333AlCl_3(g) + H_2O(g) + 2CO_2(g)$

T (°C)	ΔH (kcal)	ΔS (kcal)	ΔG (kcal)	K_{eq}
0.000	-44.076	94.797	-69.970	9.734E+055
100.000	-43.990	95.096	-79.475	3.562E+046
200.000	-44.229	94.542	-88.962	1.245E+041
300.000	-44.715	93.617	-98.372	3.262E+037
400.000	-45.399	92.520	-107.680	9.182E+034
500.000	-46.255	91.338	-116.873	1.096E+033
600.000	-47.248	90.132	-125.946	3.365E+031
700.000	-48.328	88.961	-134.900	1.988E+030
800.000	-49.475	87.840	-143.740	1.886E+029
900.000	-50.671	86.775	-152.470	2.550E+028
1000.000	-51.901	85.769	-161.097	4.532E+027

[0052] In addition to the chloride compounds, the bromide and iodide compounds of these high-k materials, such as $AlBr_3$, AlI_3, $HfBr_4$, HfI_4, $ZrBr_4$, and ZrI_4 have volatility

similar to their corresponding chlorides. Therefore, some bromo- and iodo-compounds can also be used to etch/clean these high-k materials. Bromine and iodine ions are heavier than chlorine ions, hence bromine and iodine ions can provide more effective sputtering to energize plasma-assisted etch/clean reactions with high-k materials. Bromine and iodine atoms have higher surface sticking coefficients than chlorine atoms. A higher sticking coefficient relates to a higher probability for bromine and iodine atoms/ions to be adsorbed onto the surface of high-k materials hence enhancing the bromination/iodization reactions. Desirable bromo- and iodo-compounds may contain an oxygen-getter function in the molecule. Examples of suitable bromine and iodine containing compounds include boron tribromide (BBr_3), boron triiodide (BI_3), hydrogen bromide (HBr), hydro iodide (HI), bromocarbons such as CBr_4, bromohydrocarbons such as trans-dibromoethylene ($C_2H_2Br_2$), iodocarbons such as CI_4, and iodohydrocarbons such as trans-diiodoethylene ($C_2H_2I_2$) etc. For HfO_2, the bromine and iodine chemistries are dramatically more favorable than the corresponding chlorine chemistry, as shown in tables 13-15.

Table 13 Thermodynamic data for reaction:
$1.5HfO_2 + 2BCl_3(g) = 1.5HfCl_4(g) + B_2O_3$

T (°C)	ΔH (kcal)	ΔS (kcal)	ΔG (kcal)	K_{eq}
0.000	-17.999	-12.638	-14.547	4.367E+011
100.000	-18.096	-12.924	-13.273	5.950E+007
200.000	-18.268	-13.335	-11.959	3.346E+005
300.000	-18.413	-13.614	-10.611	1.113E+004
400.000	-18.507	-13.765	-9.241	1.001E+003
500.000	-12.540	-5.525	-8.268	2.175E+002
600.000	-12.126	-5.020	-7.743	8.672E+001
700.000	-11.790	-4.655	-7.260	4.271E+001
800.000	-11.524	-4.395	-6.808	2.436E+001
900.000	-11.321	-4.213	-6.378	1.543E+001
1000.000	-11.176	-4.094	-5.963	1.056E+001

Table 14 Thermodynamic data for reaction:
$1.5HfO_2 + 2BBr_3(g) = 1.5HfBr_4(g) + B_2O_3$

T (°C)	ΔH (kcal)	ΔS (kcal)	ΔG (kcal)	K_{eq}
0.000	-53.997	-10.093	-51.241	1.003E+041
100.000	-54.122	-10.459	-50.219	2.602E+029
200.000	-54.371	-11.049	-49.143	5.026E+022
300.000	-54.601	-11.492	-48.014	2.042E+018
400.000	-54.773	-11.770	-46.850	1.629E+015
500.000	-48.872	-3.621	-46.073	1.058E+013
600.000	-48.508	-3.178	-45.734	2.806E+011
700.000	-48.207	-2.851	-45.433	1.600E+010
800.000	-47.960	-2.609	-45.161	1.577E+009
900.000	-47.761	-2.431	-44.909	2.328E+008
1000.000	-47.606	-2.304	-44.673	4.669E+007

Table 15 Thermodynamic data for reaction:
$1.5HfO_2 + 2BI_3(g) = 1.5HfI_4(g) + B_2O_3$

T (°C)	ΔH (kcal)	ΔS (kcal)	ΔG (kcal)	K_{eq}
0.000	-58.042	-15.921	-53.694	9.212E+042
100.000	-58.342	-16.842	-52.057	3.104E+030
200.000	-58.692	-17.675	-50.329	1.775E+023
300.000	-58.991	-18.250	-48.531	3.214E+018
400.000	-59.216	-18.614	-46.686	1.442E+015
500.000	-53.362	-10.530	-45.221	6.080E+012
600.000	-53.042	-10.139	-44.189	1.152E+011
700.000	-52.784	-9.859	-43.190	5.015E+009
800.000	-52.581	-9.660	-42.214	3.961E+008
900.000	-52.429	-9.524	-41.256	4.856E+007
1000.000	-52.324	-9.438	-40.308	8.315E+006

[0053] Similarly, bromine and iodine chemistries are also thermodynamically favorable for reactions with Al_2O_3 and ZrO_2, as shown in Tables 16-18.

Table 16. Thermodynamic data for reaction:
$2BBr_3(g) + Al_2O_3 = 2AlBr_3(g) + B_2O_3$

T (°C)	ΔH (kcal)	ΔS (kcal)	ΔG (kcal)	K_{eq}
0.000	-2.212	12.687	-5.678	3.493E+004
100.000	-2.279	12.503	-6.944	1.168E+004
200.000	-2.482	12.022	-8.170	5.945E+003
300.000	-2.685	11.632	-9.352	3.683E+003
400.000	-2.852	11.362	-10.501	2.567E+003
500.000	3.023	19.476	-12.035	2.525E+003
600.000	3.337	19.858	-14.003	3.200E+003
700.000	3.579	20.122	-16.003	3.928E+003
800.000	3.764	20.303	-18.024	4.688E+003
900.000	3.897	20.422	-20.061	5.464E+003
1000.000	3.985	20.494	-22.107	6.241E+003

Table 17 Thermodynamic data for reaction:
$2BBr_3(g) + 1.5ZrO_2 = 1.5ZrBr_4(g) + B_2O_3$

T (°C)	ΔH (kcal)	ΔS (kcal)	ΔG (kcal)	K_{eq}
0.000	-44.096	-11.573	-40.935	5.691E+032
100.000	-44.194	-11.861	-39.768	1.965E+023
200.000	-44.363	-12.264	-38.560	6.495E+017
300.000	-44.489	-12.509	-37.320	1.706E+014
400.000	-44.545	-12.600	-36.064	5.125E+011
500.000	-38.522	-4.282	-35.212	9.000E+009
600.000	-38.033	-3.686	-34.815	5.186E+008
700.000	-37.604	-3.220	-34.470	5.520E+007
800.000	-37.229	-2.853	-34.167	9.096E+006
900.000	-36.902	-2.561	-33.897	2.067E+006
1000.000	-36.619	-2.330	-33.653	5.989E+005

Table 18 Thermodynamic data for reaction:
$2BI_3(g) + 1.5ZrO_2 = 1.5ZrI_4(g) + B_2O_3$

T (°C)	ΔH (kcal)	ΔS (kcal)	ΔG (kcal)	K_{eq}
0.000	-74.430	-11.695	-71.235	1.001E+057
100.000	-74.587	-12.171	-70.045	1.067E+041
200.000	-74.805	-12.689	-68.801	6.053E+031
300.000	-74.972	-13.013	-67.514	5.573E+025
400.000	-75.065	-13.163	-66.204	3.134E+021
500.000	-69.074	-4.891	-65.293	2.873E+018
600.000	-68.614	-4.330	-64.833	1.695E+016
700.000	-68.212	-3.894	-64.423	2.947E+014
800.000	-67.861	-3.549	-64.052	1.110E+013
900.000	-67.555	-3.276	-63.711	7.411E+011
1000.000	-67.291	-3.061	-63.394	7.642E+010

[0054] In certain embodiments, the reactive agent may comprise a chelating compound. A chelating compound, as used herein, describes a compound that contains at least two electron-rich (e.g., Lewis base) sites that could potentially interact with an electron-deficient (e.g., Lewis acid) metal atom such as, but not limited to, Zr, Al, or Hf. It is not required, however, that the plurality of sites simultaneously interact with the metal in order. Also, the chelating compound may be delivered into the reaction chamber as a conjugate acid of the basic site. Examples of these compounds may be found in U. S. Pat. No. 3,634,477. Further examples of chelating compounds include oxy-halocarbon compounds, such as chloroacetic acid, oxalyl chloride, etc., are known to be chelating compounds or agents that can react with metal oxides and metal chlorides to form volatile byproducts. Some exemplary chelating compounds may have the formula $C_\alpha H_\beta X_\gamma Y_\delta O_\varepsilon$, wherein X and Y are one of the halogen atoms F, Cl, Br, and I; α is a number ranging from 1 to 6, β is a number ranging from 0 to 13, the sum of $\gamma + \delta$ is a number ranging from 1 to 14, and ε is a number ranging from 1 to 6. Examples of these compounds include hexafluoropetanedione ($CCl_3C(O)CH_2C(O)CCl_3$) (a.k.a. Hhfac), hexachloropetanedione ($CCl_3C(O)CH_2C(O)CCl_3$), hexafluoroacetone ($CF_3C(O)CF_3$) and hexachloroacetone ($CCl_3C(O)CCl_3$). For example, hexafluoropetanedione (a.k.a. Hhfac) ($CF_3C(O)CH_2C(O)CF_3$, or $C_5H_2O_2F_6$) is a common chelating agent that can react with a wide variety of metal oxides and/or chlorides to form volatile organo-metal compounds $M(hfac)_x$, where M is a metal ion such as Al^{3+}, Hf^{4+}, and Zr^{4+} etc. Such chelating property can be used to enhance the etching and chamber cleaning of high-k materials. In addition, these molecules can be used as an oxygen scavenger to enhance chlorination of the high-k materials. For example, one can have:

$$HfO_2 + C_5H_2O_2F_6 + 2Cl_2 + O_2 = HfCl_4(g) + H_2O(g) + 3COF_2(g) + 2CO(g)$$

[0055] In certain embodiments of the present invention, the chlorine analog of Hhfac, hexachloropetanedione ($CCl_3C(O)CH_2C(O)CCl_3$) may be more advantageous as the reactive agent since it can be both an oxygen scavenger and a chlorinating agent. These reactions can be also be assisted by thermal and/or plasma activation. For example,

$$C_5H_2O_2Cl_6 + Al_2O_3 + 0.5O_2 = 2AlCl_3(g) + 5CO(g) + H_2O(g)$$

and

$$2C_5H_2O_2Cl_6 + 3HfO_2 + O_2 = 3HfCl_4(g) + 10CO(g) + 2H_2O(g)$$

[0056] To prevent oxidation of the metal chlorides, chlorine can be used to replace oxygen:

$$C_5H_2O_2Cl_6 + Al_2O_3 + Cl_2 = 2AlCl_3(g) + 5CO(g) + 2HCl(g)$$

[0057] In certain embodiments, chlorosilanes, hydrochlorosilanes, and organochlorosilanes can also be effective agents to etch/clean high-k materials. Due in part to the highly stable SiO_2 byproduct, these compounds may be both a very effective oxygen scavenger and a chlorinating agent. Upon exposure to a thermal or plasma source, these compounds may be just as effective as BCl_3 to convert high-k materials into volatile chlorides without the potential problem of boron residue contamination. In certain embodiments, the chlorosilane, hydrochlorosilane, or organochlorosilane compound has the formula $Si_pCl_qR_sH_t$, wherein: $1 \le p \le 3$, $1 \le q \le \{2p + 2 - (s+t)\}$, s and t can have any values subject to the constraint that $0 \le (s + t) \le (2p + 1)$ and R is an organic radical having 1-8 carbon atoms, including: hydrocarbyl (e.g. methyl, ethyl, phenyl, *p*-tolyl), halocarbyl (e.g., trichloromethyl, trifluoromethyl, pentafluoroethyl), halogenated hydrocarbyl (e.g., chloromethyl, 2, 4-difluorophenyl), oxygenated hydrocarbyl (e.g., methoxy, hydroxyethyl, chlorormethoxy) and nitrogen-substituted hydrocarbyl moieties (e.g., aminomethyl, dimethylaminonomethyl, pyridyl). Exemplary reactions include:

$$1.5SiCl_4(g) + Al_2O_3 = 2AlCl_3(g) + 1.5SiO_2$$

$$SiCl_4(g) + HfO_2 = HfCl_4(g) + SiO_2$$

$$SiCl_4(g) + ZrO_2 = ZrCl_4(g) + SiO_2$$

$$O_2(g) + 2SiHCl_3(g) + Al_2O_3 = 2AlCl_3(g) + H_2O(g) + 2SiO_2$$

$$4O_2(g) + 2SiCH_3Cl_3(g) + Al_2O_3 = 2AlCl_3(g) + 3H_2O(g) + 2SiO_2 + 2CO_2(g)$$

Thermodynamic calculations show that the above reactions are favorable at room temperature or moderately elevated temperatures, as shown in Tables 19-23.

Table 19 Thermodynamic data for reaction:
$1.5SiCl_4(g) + Al_2O_3 = 2AlCl_3(g) + 1.5SiO_2$

T (°C)	ΔH (kcal)	ΔS (kcal)	ΔG (kcal)	K_{eq}
0.000	32.037	34.471	22.621	7.927E-019
100.000	31.880	33.990	19.196	5.703E-012
200.000	31.647	33.439	15.825	4.895E-008
300.000	31.400	32.967	12.506	1.702E-005
400.000	31.178	32.608	9.228	1.009E-003
500.000	31.009	32.373	5.980	2.039E-002
600.000	31.097	32.475	2.742	2.059E-001
700.000	30.702	32.047	-0.484	1.285E+000
800.000	30.291	31.645	-3.669	5.587E+000
900.000	30.612	31.957	-6.878	1.912E+001
1000.000	30.204	31.623	-10.057	5.327E+001

Table 20 Thermodynamic data for reaction:
$SiCl_4(g) + HfO_2 = HfCl_4(g) + SiO_2$

T (°C)	ΔH (kcal)	ΔS (kcal)	ΔG (kcal)	K_{eq}
0.000	2.985	6.373	1.244	1.010E-001
100.000	2.825	5.878	0.631	4.267E-001
200.000	2.636	5.430	0.067	9.314E-001
300.000	2.459	5.089	-0.458	1.495E+000
400.000	2.317	4.860	-0.955	2.042E+000
500.000	2.230	4.739	-1.434	2.543E+000
600.000	2.330	4.857	-1.911	3.009E+000
700.000	2.110	4.618	-2.385	3.432E+000
800.000	1.877	4.391	-2.835	3.779E+000
900.000	2.130	4.633	-3.306	4.129E+000
1000.000	1.892	4.439	-3.759	4.419E+000

Table 21 Thermodynamic data for reaction:
$SiCl_4(g) + ZrO_2 = ZrCl_4(g) + SiO_2$

T (°C)	ΔH (kcal)	ΔS (kcal)	ΔG (kcal)	K_{eq}
0.000	-4.912	6.726	-6.749	2.516E+005
100.000	-5.006	6.439	-7.408	2.185E+004
200.000	-5.123	6.160	-8.038	5.164E+003
300.000	-5.226	5.963	-8.643	1.977E+003
400.000	-5.288	5.861	-9.233	9.955E+002
500.000	-5.292	5.854	-9.818	5.966E+002
600.000	-5.106	6.077	-10.412	4.041E+002
700.000	-5.237	5.936	-11.013	2.975E+002
800.000	-5.375	5.800	-11.600	2.304E+002
900.000	-5.026	6.129	-12.216	1.887E+002
1000.000	-5.163	6.016	-12.823	1.590E+002

Table 22 Thermodynamic data for reaction:
$O_2(g) + 2SiHCl_3(g) + Al_2O_3 = 2AlCl_3(g) + H_2O(g) + 2SiO_2$

T (°C)	ΔH (kcal)	ΔS (kcal)	ΔG (kcal)	K_{eq}
0.000	-134.894	4.620	-136.156	8.893E+108
100.000	-135.412	2.993	-136.529	9.339E+079
200.000	-135.834	1.989	-136.775	1.521E+063
300.000	-136.187	1.309	-136.938	1.662E+052
400.000	-136.464	0.863	-137.045	3.145E+044
500.000	-136.643	0.612	-137.117	5.789E+038
600.000	-136.462	0.826	-137.183	2.187E+034
700.000	-136.917	0.333	-137.241	6.669E+030
800.000	-137.387	-0.126	-137.251	8.991E+027
900.000	-136.875	0.364	-137.301	3.806E+025
1000.000	-137.329	-0.008	-137.319	3.752E+023

Table 23 Thermodynamic data for reaction:
$4O_2(g) + 2SiCH_3Cl_3(g) + Al_2O_3 = 2AlCl_3(g) + 3H_2O(g) + 2SiO_2 + 2CO_2(g)$

T (°C)	ΔH (kcal)	ΔS (kcal)	ΔG (kcal)	K_{eq}
0.000	-423.175	31.434	-431.762	1.000E+308
100.000	-423.093	31.710	-434.925	5.650E+254
200.000	-423.197	31.470	-438.087	2.349E+202
300.000	-423.424	31.038	-441.213	1.797E+168
400.000	-423.714	30.573	-444.294	1.818E+144
500.000	-424.016	30.154	-447.329	2.878E+126
600.000	-424.028	30.132	-450.339	5.361E+112
700.000	-424.723	29.380	-453.314	6.510E+101
800.000	-425.461	28.658	-456.216	8.264E+092
900.000	-425.237	28.892	-459.132	3.469E+085
1000.000	-425.990	28.276	-461.990	2.051E+079

[0058] In addition, other chloride compounds such as $GeCl_4$ and related compounds can also be used to etch/clean high-k materials in a similar manner. When etching/cleaning hafnium and zirconium based high-k materials, $AlCl_3$ can be added into the reactants to enhance the chlorination of HfO_2, ZrO_2, $HfSi_xO_y$, and $ZrSi_xO_y$ etc. This is because $AlCl_3$ can be used as an oxygen scavenger to facilitate the chlorination of HfO_2 and ZrO_2 etc. while forming aluminum oxychloride such as AlOCl, which is more volatile than Al_2O_3.

[0059] In addition to being thermodynamically favorable, a chemical reaction often requires an external energy source to overcome an activation energy barrier so that the reaction can proceed. The external energy source can be, for example, thermal heating or plasma activation. Higher temperatures can accelerate chemical reactions and make

reaction byproducts more volatile. However, there may be practical limitations on temperature in production deposition chambers. Plasmas can generate more reactive species to facilitate reactions. Ions in the plasmas are accelerated by the electric field in the plasma sheath to gain energy. Energetic ions impinging upon surfaces can provide the energy needed to overcome reaction activation energy barrier. Ion bombardments also helps to volatize and remove reaction byproducts. These are common mechanisms in plasma etching/cleaning and reactive ion etching. Optionally, one can combine both thermal and plasma activation mechanisms to enhance the desired reactions for dry etching/cleaning of high-k materials. As an alternative to in situ plasma cleaning, one can use remote plasma source to generate more reactive species for cleaning high-k material residues from the deposition chambers. In addition, reactions between remote plasma generated reactive species and high-k materials can be activated and/or enhanced by heating CVD or ALD reactor components to elevated temperatures up to 600 °C, or to 400 °C, and or up to 300 °C.

[0060] Figures 1a and 1b provides an illustration of an apparatus 10 suitable for performing chamber cleaning using an internal energy source such as an in-situ plasma or a thermal source or an external energy source, respectively. In Figure 1a, the reactive agent 20 (i.e., BCl_3) (depicted in Figure 1a as solid arrows) is introduced into the substrate 30 (i.e., reaction chamber), which has the substance 40 to be removed, or the high-k residues such as the HfO_2 depicted. As shown in Figure 1a, the substance 40 is deposited upon at least a portion of the exposed surface within the reaction chamber 30, particularly, the grounded sidewalls 32, showerhead 34, work piece platform 36, etc. The reactive agent 20 is exposed to an external energy source 50, such as the RF power supply or heater shown, which creates active species 60 such as BCl_3 and Cl shown by the dashed arrows. The active species 60 react with substance 40 and form a volatile product 70 such as $HfCl_4$. The volatile product 70 is removed from the chamber 30 as shown by the dotted arrows.

[0061] Figure 1b provides an example of an apparatus 100 wherein the reactive agent 120 (i.e., BCl_3) is exposed to an external energy source 150 such as a microwave source to produce a high density plasma 110 of the reactive agent within an applicator/resonant cavity 115. The high density plasma 110 can then be transported to the substrate 130 (i.e., reaction chamber) having the substance to be removed (not shown) and form the volatile product (not shown). The volatile product can be easily removed from the chamber 130 via the foreline shown 140 and assisted by pump 160.

EXAMPLES

[0062] The invention will be illustrated in more detail with reference to the following Examples, but it should be understood that the present invention is not deemed to be limited thereto.

[0063] The following are experimental examples of utilizing the above chemistries for dry etching/cleaning of high-k materials. The experiments for examples 1 through 3 were conducted in a parallel plate capacitively coupled RF plasma reactor similar to the setup illustrated in Fig. 2. Sample coupons 200 were prepared from wafers coated with high-k dielectric materials Al_2O_3, HfO_2, and ZrO_2 deposited by atomic layer deposition. For each experimental run, a sample coupon 200 was put onto a carrier wafer 210 and loaded onto the reactor chuck 220 through a loadlock 230. Process gases 240 were fed into the reactor 250 from a top mounted showerhead 255. The chuck 220 was then powered by a 13.56 MHz RF power source 260 to generate the plasma (not shown). Reactor 250 is connected to a turbo pump (not shown) through line 270. The thickness of the high-k film on a coupon was measured by ellipsometry both before and after a timed exposure of the processing plasma. Change in high-k film thickness after plasma processing is used to calculate the etch rate. In addition to etch rate, plasma dc self bias voltage (V_{bias}) was also measured. In examples 1-3, both the wafer and the chamber walls were kept at room temperature.

Example 1: Plasma etching/cleaning of Al_2O_3 samples

[0064] Since power is one of the key processing parameters in plasma etching/cleaning, we evaluated power dependence of Al_2O_3 etching by BCl_3 plasma. The results are listed in Table 24 below.

Table 24. RF power dependence of Al_2O_3 etching by BCl_3 plasma

Power (W)	Power density (W/cm^2)	Pressure (mTorr)	Al_2O_3 etch rate (nm/min)	V_{bias} (V)
50	0.27	500	0.0	16
100	0.55	500	3.0	35
200	1.10	500	9.8	58

[0065] Apparently there is a threshold power density of 0.55 W/cm^2 or threshold V_{bias} of 35 V for etching Al_2O_3. Higher power density and higher V_{bias} resulted in higher etch rate.

[0066] Next, we investigated chamber pressure dependence of Al_2O_3 etching by BCl_3 plasma. The results are listed in Table 25 below.

Table 25. Chamber pressure dependence of Al_2O_3 etching by BCl_3 plasma

Power (W)	Power density (W/cm^2)	Pressure (mTorr)	Al_2O_3 etch rate (nm/min)	V_{bias} (V)
100	0.55	50	7.2	91
100	0.55	500	3.0	35
100	0.55	1000	0.8	4

[0067] A higher etch rate was achieved at a reduced pressure. There are two factors that favor the etch reactions at reduced pressure. First, higher bias voltage at lower pressure leads to more energetic ion bombardment to help the etch reactions to overcome activation energy barrier. Second, lower pressure leads to faster desorption and diffusion of reaction byproducts. Higher V_{bias} also enhances physical sputtering by energetic ions. To delineate the contributions from reactive ion etching and physical sputtering, we conducted comparison runs using pure argon plasma. The results are listed in Table 26 below.

Table 26. Argon plasma etching of Al_2O_3

Power (W)	Power density (W/cm^2)	Pressure (mTorr)	Al_2O_3 etch rate (nm/min)	V_{bias} (V)
200	1.10	5	0.6	173
200	1.10	50	1.0	189
200	1.10	500	-0.4	185

[0068] The data showed pure argon plasma essentially did not etch Al_2O_3 even with very high power and a relatively higher V_{bias} than that of BCl_3 plasmas. This indicates that physical sputtering may not be the primary mechanism to etch Al_2O_3. Instead, ion bombardment enhanced chemical etching, or reactive ion etching (RIE) may be the primary mechanism.

[0069] At a fixed RF excitation frequency (such as 13.56 MHz), the data in Tables 24 and 25 show, for example, that higher power and lower pressure can increase bias voltage, which in turn may enhance chemical etching of high-k materials. Lower pressure and higher power is particularly effective to enhance plasma etching of substrates coated with high-k films.

[0070] One can also operate the RF plasma at lower frequencies. Ions transiting through a plasma sheath often exhibit a bi-modal energy distribution at lower frequencies. Bimodal ion energy distribution results in a large fraction of the ions impinging onto reactor surfaces with higher energies. This can be an effective strategy to enhance plasma cleaning of high-k deposition residues from grounded ALD chamber surfaces.

Example 2: Plasma etching/cleaning of HfO_2 samples

[0071] At 500 mTorr pressure, etching of HfO_2 was achieved at all power levels between 50 and 200 W. The results are listed in Table 27 below.

Table 27. BCl_3 plasma etching of HfO_2

Power (W)	Power density (W/cm^2)	Pressure (mTorr)	HfO_2 etch rate (nm/min)	V_{bias} (V)
50	0.27	500	1.6	14
50	0.27	500	1.4	16
100	0.55	500	4.7	34
200	1.10	500	14.7	63

Example 3: Plasma etching/cleaning of ZrO_2 samples

[0072] Several experiments were conducted with ZrO_2 samples using 500 mTorr pressure and various power levels between 50 and 200 W. The results are listed in Table 28 below.

Table 28. BCl_3 plasma etching of ZrO_2

Power (W)	Power density (W/cm^2)	Pressure (mTorr)	ZrO_2 etch rate (nm/min)	V_{bias} (V)
50	0.27	500	0.3	16
100	0.55	500	-3.8*	32
100	0.55	500	-2.5*	45
200	1.10	500	7.1	65

* The film became thicker after one minute exposure to the plasma.

[0073] Figure 3 shows the relative comparison of BCl_3 plasma etch rates of high-k materials HfO_2, Al_2O_3, and ZrO_2 at 500 mTorr chamber pressure and 1 W/cm^2 RF power density. It can be seen that HfO_2 has the highest etch rate, and ZrO_2 has the lowest etch rate among the three high-k materials.

[0074] Examples 4 and 5 illustrate BCl_3 thermal etching/cleaning of high-k materials. Figure 4 is a schematic of the experimental setup for examples 4 and 5. In this reactor chamber 300, RF power 310 can be applied on the top electrode 320, and the lower electrode 330 and the chamber walls 340 are grounded. This reactor can be operated with both RF plasma and thermal heating during an etching/cleaning experiments. Only thermal heating was used in examples 4 and 5. The lower electrode/pedestal 330 can be heated by an AC powered heater 350 and controlled by the temperature controller 360. The temperature range of the lower electrode/pedestal 330 is from room temperature up to 700°C. The sample 360 and the carrier wafer 370 were placed on the lower electrode/pedestal 330. Sample surface temperature is about 50°C lower than the lower electrode set point in ambient atmosphere. Sample preparation and measurement procedures were similar to those in examples 1 through 3. After sample introduction, the reactor was evacuated, and the heater 350 was turned on. When the lower electrode 330 reached the set point, process gases 380 were introduced into the chamber 300 to reach a set pressure. The sample was exposed to the process gases 380 for a set period of time. The process gases 380 were evacuated through line 390 that connects to a pump (not shown) and the sample 360 was retrieved from the reactor chamber 300 for measurement.

Example 4: Thermal etching/cleaning of Al_2O_3 samples

[0075] Several experiments were conducted using BCl_3 as the etchant for thermal etching/cleaning of Al_2O_3 samples. The process variables were lower electrode temperature, chamber pressure, and BCl_3 flow rate. The results are listed in Table 29.

Table 29 BCl_3 thermal etching of Al_2O_3

Lower Electrode Set Temperature (°C)	Chamber Pressure (Torr)	BCl_3 Flow Rate (sccm)	Etch Rate (nm/min)
200	100	100	0.0
350	25	100	0.1
350	100	100	0.2
350	100	100	0.2
350	100	0	0.3
350	200	100	0.3
350	400	100	0.7
600	100	100	0.6

Example 5: Thermal etching/cleaning of HfO_2 samples

[0076] A similar set of experiments were conducted using BCl_3 as the etchant for thermal etching/cleaning of HfO_2 samples. The process variables were lower electrode temperature, chamber pressure, and BCl_3 flow rate. The results are listed in Table 30.

Table 30 BCl_3 thermal etching of HfO_2

Lower Electrode Set Temperature (°C)	Chamber Pressure (Torr)	BCl_3 Flow Rate (sccm)	Etch Rate (nm/min)
200	100	100	0.0
350	25	100	0.1
350	100	100	0.6
350	100	100	0.6
350	100	0	0.6
350	200	100	1.1
350	400	100	2.4
600	100	100	1.1

[0077] Figure 5 examines the etch rate dependence on lower electrode temperature at constant chamber pressure and BCl_3 flow rate. It can be seen that both Al_2O_3 and HfO_2 etch rates increase at temperature increases. The etch rates of HfO_2 are higher than those of Al_2O_3 under the same conditions.

[0078] Figure 6 examines the etch rate dependence on chamber pressure at constant lower electrode set temperature and BCl_3 flow rate. It can be seen that etch rates increase at higher pressures. At lower electrode temperature about 350°C, increasing chamber pressure is a more effective method to enhance etch rates. Again, the etch rates of HfO_2 are higher than those of Al_2O_3 under the same conditions.

[0079] The data in Tables 29 and 30 shows that there is no strong dependence between etch rate and BCl_3 flow rate. This means one can operate thermal etching/cleaning either with continuous flow of etchant gases (such as BCl_3) or with static chamber at a set pressure without flow.

Comparative Example 1: NF_3 plasma etching/cleaning of Al_2O_3, HfO_2, and ZrO_2 samples

[0080] A set of plasma experiments were conducted using a mixture of 8.7 standard cubic centimeter (sccm) NF_3 and 49.3 sccm He in the same apparatus as shown in Figure 2 and following the same method as Examples 1 through 3. Three different high-k materials, Al_2O_3, HfO_2, and ZrO_2, were tested at a variety of power density and chamber pressure. Detailed experimental conditions and results are provided in Table 31. As the results in Table 31 show, higher power density and reduced chamber pressure resulted in a higher etch rate. In certain cases, there was a higher bias voltage, which lead to more energetic ion bombardment to help the etch reactions to overcome activation energy barrier and enhances physical sputtering by energetic ions. A lower chamber pressure may also lead to faster desorption and diffusion of reaction byproducts. Compared to BCl_3 plasma experimental results in the preceding examples, the NF_3 plasma had significantly lower etch rates for either the Al_2O_3, the HfO_2, or the ZrO_2 samples.

Table 31: NF_3 plasma etching of Al_2O_3, HfO_2, and ZrO_2

Samples	Power Density (W/cm^2)	Pressure (mTorr)	Etch Rate (nm/min)	V_{bias} (V)
Al_2O_3	1.1	100	11	590
Al_2O_3	1.1	250	4	541
Al_2O_3	1.1	500	2	456
Al_2O_3	1.1	1000	0.1	310
Al_2O_3	0.55	500	0.1	260
Al_2O_3	0.27	500	0	130
HfO_2	1	250	5	550
HfO_2	1	500	4	456
HfO_2	1	1000	-0.2	310
HfO_2	0.55	500	0.3	260
HfO_2	0.27	500	-0.1	130
ZrO_2	1	500	1	456
ZrO_2	1	1000	-0.2	310
ZrO_2	0.55	500	0.1	260
ZrO_2	0.27	500	0	130

Example 6: Plasma Etching/Cleaning of HfO_2, ZrO_2, and $HfSi_xO_y$ samples using a mixture of BCl_3 and NF_3

[0081] A mixture of BCl_3 and NF_3 was used to test the etch rates of three different high-k materials, HfO_2, ZrO_2, and $HfSi_xO_y$. For HfO_2, the flow rate of BCl_3 was 10 sccm and the flow rate of NF_3 was adjusted to obtain different NF_3 to BCl_3 volumetric ratios. For ZrO_2 and $HfSi_xO_y$, the total flow rate was 20 sccm and the flow rates of BCl_3 and NF_3 were adjusted accordingly to obtain different NF_3 to BCl_3 volumetric ratios. For all experimental runs, the power density was 0.55 W/cm^2 and the chamber pressure was 500 mTorr. The experiments were run using the same set-up as shown in Figure 2 and following the same method as Examples 1 through 3 and Comparative Example 1.

[0082] Figures 7a through 7c illustrate the relationship between the volumetric percentage of NF_3 in the BCl_3 and NF_3 mixture and etch rates for HfO_2, $HfSi_xO_y$, ZrO_2, respectively. Compared to pure BCl_3, the etch rates for HfO_2 (shown in Figure 7a) and for $HfSi_xO_y$ (shown in Figure 7b) were almost doubled at about 25% by volume NF_3 and 15% by volume NF_3, respectively.

[0083] Figure 7c shows the etch rates of ZrO_2 at different NF_3 additions to BCl_3. Without NF_3, BCl_3 cannot remove the ZrO_2 material under the given plasma condition: 0.55 W/cm^2 power density and 500 mTorr reactor chamber pressure. In fact, the thickness of ZrO_2 was increased after 1-minute exposure to the BCl_3 plasma. Etching,

however, occurs with addition of NF_3. Similar to HfO_2 and $HfSi_xO_y$, there is a maximum etch rate for ZrO_2 at about 20% by volume NF_3.

[0084] While the invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

CLAIMS

1. A process for cleaning a substance from a reactor surface, said process comprising:

providing a reactor containing the reactor surface, wherein: (a) the reactor surface is at least partially coated with a film of the substance; (b) the substance is at least one member selected from the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing Group 13 metal oxide, a nitrogen containing Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, or a laminate comprising at least one layer selected from the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, a nitrogen containing Group 13 metal oxide, or a nitrogen containing Group 13 metal silicate; and (c) the substance has a dielectric constant greater than the dielectric constant of silicon dioxide;

reacting the substance with a reactive agent to form a volatile product, wherein the reactive agent comprises at least one member selected from the group consisting of a halogen-containing compound; a boron-containing compound, a carbon-containing compound, a hydrogen-containing compound, a nitrogen-containing compound, a chelating compound, a chlorosilane compound, a hydrochlorosilane compound, or an organochlorosilane compound; and

removing the volatile product from the reactor to thereby remove the substance from the surface.

2. The process of claim 1, wherein the reactor is an atomic layer deposition reactor.

3. The process of claim 1, wherein the substance is at least one member selected from the group consisting of Al_2O_3, HfO_2, ZrO_2, $HfSi_xO_y$, and

$ZrSi_xO_y$ wherein x is a number greater than 0 and y is 2x + 2, and any of the aforementioned compounds containing nitrogen.

4. The process of claim 1, wherein the reactive agent is at least one member selected from the group consisting of BCl_3, $COCl_2$, HCl, Cl_2, ClF_3, NF_3, F_2, and NF_zCl_{3-z}, where z is an integer from 0 to 2.

5. The process of claim 4, wherein the reactive agent is $COCl_2$ formed by an in situ reaction of CO and Cl_2.

6. The process of claim 4, wherein the reactive agent is BCl_3.

7. The process of claim 1, wherein the reactive agent is a carbon-containing compound having the formula $C_xH_yCl_z$, wherein x is a number ranging from 1 to 6, y is a number ranging from 0 to 13, and z is a number ranging 1 from 14.

8. The process of claim 1, wherein the reactive agent is conveyed to the substance from a gas cylinder, a safe delivery system or a vacuum delivery system.

9. The process of claim 1, wherein the reactive agent is formed in situ by a point-of-use generator.

10. The process of claim 1, wherein the substance is contacted with the reactive agent diluted with an inert gas diluent.

11. The process of claim 1, wherein the reactive agent comprises a mixture of halogen-containing compounds.

12. The process of claim 11, where the mixture of halogen-containing compounds comprises at least one chlorine-containing gas and less than 50% by volume of at least one fluorine-containing gas.

13. The process of claim 1, wherein the reactive agent is deposited onto a nonreactive support.

14. An apparatus for removing a substance from at least one surface of a reactor, the apparatus comprising:

an at least one reactive agent selected from the group consisting of a halogen-containing compound; a boron-containing compound, a carbon-containing compound, a hydrogen-containing compound, a nitrogen-containing compound, a chelating compound, a chlorosilane compound, a hydrochlorosilane compound, or an organochlorosilane compound; and

a non-reactive support having the at least one reactive agent deposited thereupon.

15. A mixture for removing a substance from at least one surface of a reactor, the mixture comprising:

an at least one reactive agent selected from the group consisting of a halogen-containing compound; a boron-containing compound, a carbon-containing compound, a hydrogen-containing compound, a nitrogen-containing compound, a chelating compound, a chlorosilane compound, a hydrochlorosilane compound, or an organochlorosilane compound; and

an inert diluent.

16. A process for removing a substance from an at least one surface of a substrate, said process comprising:

providing the substrate wherein the substrate is at least partially coated with a film of the substance that is at least one member selected from the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide other than Al_2O_3, a Group 13 metal silicate, a nitrogen containing Group 13 metal oxide, a nitrogen containing Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, or a laminate comprising at least one layer of the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing Group 13 metal oxide, a nitrogen containing Group 13 metal silicate, a nitrogen containing transition metal oxide, or a nitrogen containing transition metal silicate; and wherein the substance has a dielectric constant greater than a dielectric constant of silicon dioxide;

reacting the substance with a reactive agent to form a volatile product, wherein the reactive agent comprises at least one member from the group consisting of a halogen-containing compound; a boron-containing compound, a carbon-containing compound, a hydrogen-containing compound, a nitrogen-containing compound, a chelating compound, a chlorosilane compound, a hydrochlorosilane compound, or an organochlorosilane compound; and

removing the volatile product from the substrate to thereby remove the substance from the substrate.

17. The process of claim 16, wherein the substance is at least one member selected from the group consisting of HfO_2, ZrO_2, $HfSi_xO_y$, $ZrSi_xO_y$, where x is greater than 0 and y is 2x + 2, $Al_2Si_wO_z$, where w is greater than 0 and z is 2w + 3, or any of the aforementioned compounds containing nitrogen.

18. The process of claim 16, wherein the substance is a laminate comprising layers of at least one material selected from the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, a nitrogen containing Group 13 metal oxide, or a nitrogen containing Group 13 metal silicate.

19. The process of claim 16, wherein the reactive agent is at least one member selected from the group consisting of BCl_3, $COCl_2$, HCl, Cl_2, ClF_3, NF_3, F_2, and NF_zCl_{3-z}, where z is an integer from 0 to 2.

20. The process of claim 16, wherein the substance is at least one member selected from the group consisting of HfO_2, ZrO_2, $HfSi_xO_y$, $ZrSi_xO_y$, where x is greater than 0 and y is 2x + 2, $Al_2Si_wO_z$, where w is greater than 0 and z is 2w + 3, or any of the aforementioned compounds containing nitrogen.

21. A process for cleaning a substance from a reactor surface, said process comprising:

providing a reactor containing the reactor surface, wherein: (a) the reactor surface is at least partially coated with a film of the substance; (b) the substance is at least one member selected from the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing Group 13 metal oxide, a nitrogen containing Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, or a laminate comprising at least one layer selected from the group consisting of a transition metal oxide, a transition metal silicate, a Group 13 metal oxide, a Group 13 metal silicate, a nitrogen containing transition metal oxide, a nitrogen containing transition metal silicate, a nitrogen containing Group 13 metal oxide, or a nitrogen containing Group 13 metal silicate; and (c) the substance has a dielectric constant greater than the dielectric constant of silicon dioxide;

reacting the substance with a reactive agent comprising at least one fluorine-containing compound and at least one halogen-containing compound selected from a chlorine-containing compound, a bromine-containing compound, or an iodine-containing compound wherein the amount of fluorine-containing compound is less than 50% by volume of an amount of the halogen-containing compound; and

removing the volatile product from the reactor to thereby remove the substance from the surface.

22. The process of claim 1, wherein the reacting step comprises: introducing the reactive agent into the reactor chamber; and exposing the reactive agent to one or more energy sources.

23. The process of claim 22 wherein the reactive agent is exposed to one or more energy sources and the exposing step is conducted prior to the introducing step.

24. The process of claim 22, wherein the reactive agent is exposed to one or more energy sources and the exposing step is conducted during at least a portion of the introducing step.